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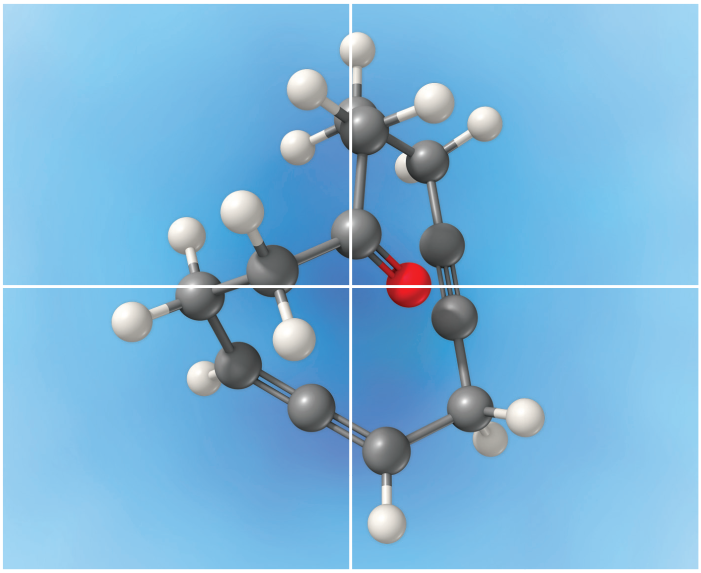

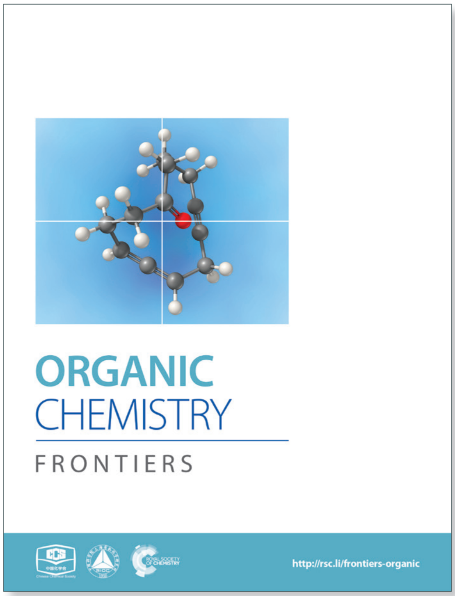

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Donor-acceptor interaction-driven folding of linear naphthalene-glycol oligomers templated by a rigid bipyridinium rod

Tian-Guang Zhan,[a‡] Ben-Ye Lu,[b‡] Feng Lin,[a] Tian-You Zhou,[a] Xin Zhao*[a] and Zhan-Ting Li*[a,b]

This paper reports the construction of folded and helical supramolecular structures through the self-assembly of a series of flexible linear donor oligomers induced by a rigid rod-like acceptor template. The donor oligomers were constructed by connecting two, four, six, and eight 1, 5-dioxynaphthalene (DAN) units with polyether chains, respectively, and the acceptor template was generated by incorporating 4, 4'-bipyridine moieties on the 3, 6 positions of a pyridazine skeleton. ^{1}H NMR, UV-vis, and fluorescence spectroscopic studies indicated that the formation of the folded and helical structures was mainly driven by the intermolecular donor-acceptor interactions between the electron-rich DAN units and the electron-deficient template, which was further supported by DFT calculations. It was also found that the strength of the interactions between the donor oligomers and acceptor template remarkably increased with the elongation of the oligomers.

Introduction

Artificial molecules that adopt folded secondary structures, widely known as foldamers,[1] represent a very rich and active field of research.[2] Since the twists and folds of biomolecules explicitly underpin their functions, the task of imparting synthetic molecules with folded secondary structures should have enormous potentials to fabricate functional materials with novel and emergent properties. Currently the most general strategy to construct a foldamer is to incorporate all bonding sites into a linear structure in a way that these bonding sites intramolecularly bind together to induce a folded or helical structure, which can be defined as internal induction. On the basis of this principle, a variety of helical or folded architectures have been established through the use of different non-covalent interactions such as hydrogen-bonding,[3] coordination interaction,[4] donor-acceptor interaction,[5] and radical dimerization.[6] On the other hand, a flexible linear structure could also evolve into a well-defined secondary structure through external induction approach if a suitable template is provided. Such externally induced formation of secondary structures has already been well demonstrated by Nature. A common example is the twisted growth of some liana round tree trunks. However, artificial folded and helical architectures constructed through this approach are quite limited.[7] It could be attributed to the challenge to design templates which can efficiently induce the formation of well-defined secondary structures. For the foldamer–rod host-guest structures, only a few examples have been reported by Jiang and Huc et al. and Moore and co-workers, in which the foldamers were constructed by hydrogen-bonding and solvophobic effect, respectively.[8]

As one of the most important non-covalent interactions in the field of supramolecular chemistry, donor-acceptor interaction, which occurred between π-electron-rich and π-electron-deficient aromatic systems, has been widely used in the design of various supramolecular architectures. Stoddart et al. have utilized donor-acceptor interaction between DAN and viologen derivatives to induce the formation of interlocked supermolecules,[9] oligomeric pseudorotaxanes,[10] and three-dimensional frameworks.[11] By using aromatic stacking between the π-electron-deficient diimide segments and the π-electron-rich pyrenyl units, Colquhoun and co-workers has established the motif of molecular tweezers[12] and further used them for the recognition of sequence information[13] and healable supramolecular polymer.[14] In spite of these progress, using donor-acceptor interaction as the main driven force to construct folded/helical structures is still a great challenge. Compared to hydrogen-bonding which has been widely used to constructed foldamers, donor-acceptor interaction exhibits weak bonding strength and less directivity. These weak points dramatically limit its application in the construction of well-defined secondary structures.

In this work, we demonstrate the induced formation of folded and helical structures from a series of flexible linear

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[a] Key Laboratory of Synthetic and Self-Assembly Chemistry for Organic Functional Molecules, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Road, Shanghai 200032, China, Email: xzhao@sioc.ac.cn

[b] Department of Chemistry, Fudan University, 220 Handan Road, Shanghai 200433, China, Email: ztli@sioc.ac.cn

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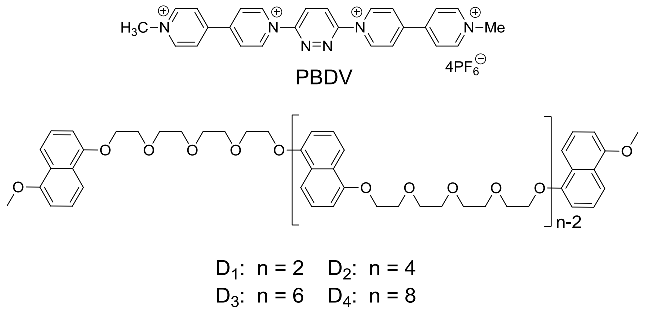
‡ These authors contributed equally to this work.



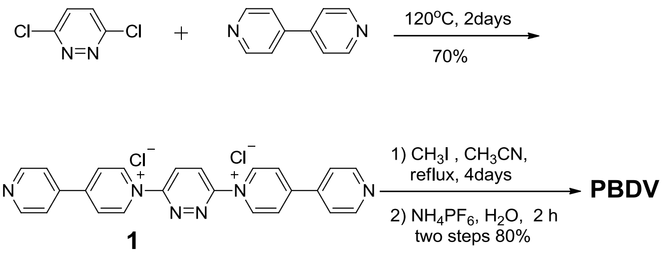
Scheme 1 Structures of **PBDV** and oligomers **D$_1$-D$_4$**.

oligomers driven by donor-acceptor interaction. The linear oligomers were constructed through connecting different numbers of electron-rich 5-dialkoxynaphthalene (DAN) units by oligoethyleneglycol (**D$_1$-D$_4$**, Scheme 1). In order to enhance inducing efficiency, a rigid rod-like tetracationic pyridazine-bridged diviologen (**PBDV**) was designed as template, in which the two viologen units make **PBDV** a highly electron-deficient molecule. The complexes formed between **PBDV** and the donor oligomers **D$_1$-D$_4$** have been studied by (1D and 2D) ^{1}H NMR, UV-vis and fluorescence spectroscopies, as well as DFT calculations, which confirmed the formation of supramolecular donor-acceptor complexes in which the flexible linear donor oligomers twined round the rigid rod-like acceptor. Furthermore, an increased stability of the as-formed complexes with the increasing number of DAN units in the oligomers was also observed.

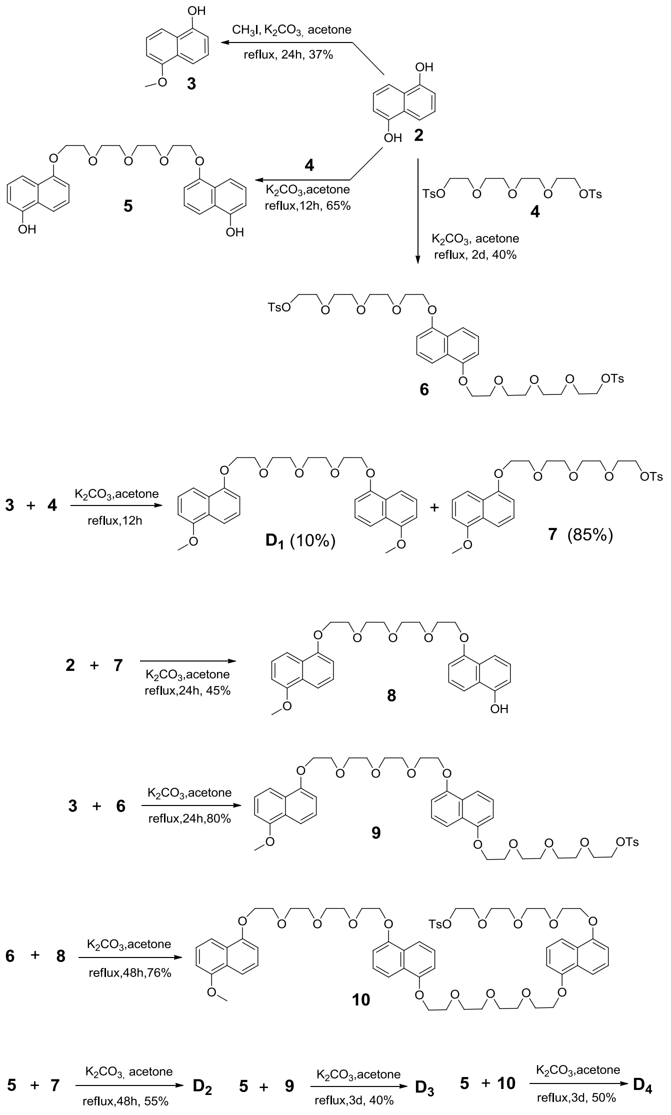
Results and discussion

The synthetic route for **PBDV** is illustrated in Scheme 2. Commercially available reactants 3, 6-dichloropyridazine and 4, 4'-bipyridine were sealed in a Shrek tube without solvent and then heated to 120 ^{o}C for 2 days under an argon atmosphere. The resulting dicationic intermediate **1** was obtained as a chloride salt, which was further treated with iodomethane in anhydrous CH_3CN to yield the target compound **PBDV** in 80% yield after anion exchange with ammonium hexafluorophosphate.

For the synthesis of donor oligomers **D$_1$-D$_4$** (Scheme 3), their corresponding intermediates **3**, **5** and **6** were firstly obtained in the yields of 37%, 40% and 65%, respectively, starting from 1,5-dioxynaphthalene and compound **4**.



Scheme 2 The synthetic route to **PBDV**.



Scheme 3 The synthetic routes to donor oligomers **D$_1$–D$_4$**.

Refluxing a mixture of **3** and **4** in the presence of K_2CO_3 afforded **D$_1$** in 10% yield while compound **7** was obtained as the major product. Compound **7** was further converted to **8** upon the treatment of **2**. Similarly, intermediates **9** and **10** were obtained by the reactions of **6** with **3** and **8**, respectively. With these intermediates in hand, oligomers **D$_2$-D$_4$** were prepared through refluxing compound **5** with **7**, **9**, and **10**, respectively. All the compounds have been fully characterized by ^{1}H and ^{13}C NMR, and (HR) mass spectroscopy, on the basis of which their chemical structures were unambiguously assigned (see ESI for the data).

The interactions between **PBDV** and **D$_1$-D$_4$** were firstly investigated by ^{1}H NMR spectroscopy. Since **D$_4$** displayed a poor solubility in CD_3CN, a mixture of CD_3CN and $CDCl_3$ (v/v, 4:1) was used as solvent. Upon mixing **PBDV** and different DAN oligomers, the signals of the aromatic protons (except Hc) of viologen unit and the methyl protons (H_f) in **PBDV** were shifted upfield (Figure 1a and Figures S1-S4, ESI). The changes of the chemical shifts of the protons are summarized in Figure 1b. It

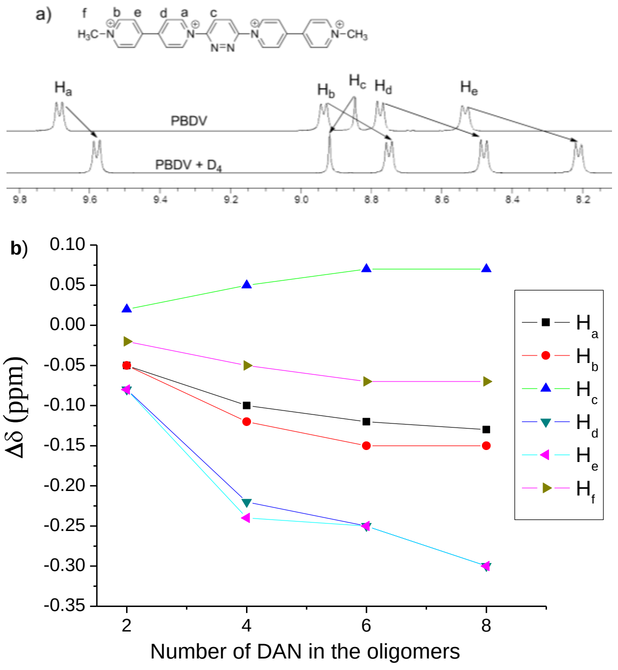


Fig. 1 (a) Partial ^1H NMR spectra of **PBDV** and 1:1mixture of **PBDV** and $\mathbf{D_4}$ in $CD_3CN/CDCl_3$ (4:1), and (b) chemical shift changes of the protons in **PBDV** after it being mixed with equivalent $\mathbf{D_4}$ in a binary solvent of CD_3CN-$CDCl_3$ (v/v, 4:1) at 20°C. The concentration of **PBDV** was 3.0 mM.

revealed that the chemical shift changes become significant when the number of DAN units increased in the oligomers, indicating an enhancement of donor-acceptor interaction between the **PBDV** and DAN upon the enlongation of the donor molecules. This result indicated the formation of complex driven by the multiple donor-acceptor interactions between **PBDV** and DAN. Similar trends for the changes of chemical shifts of the protons were also observed when kept the DAN unit of the oligomers at a same concentration (Figure S5, ESI), indicating again that the more DAN units were involved, the stronger donor-acceptor interaction generated.

It is well known that charge-transfer (CT) complex could be formed between electro-deficient viologen unit and electro-rich species such as DAN, and it could be identified by the characteristic CT absorption band usually appearing in visible range of a UV-vis spectrum.[15] UV-vis spectroscopy was thus used to confirm the formation of donor-acceptor complexes. As can be seen in Figure 2, while **PBDV** and $\mathbf{D_1}$-$\mathbf{D_4}$ only exhibit absorptions below 450 nm, new absorption peaks centred at 570 nm could be observed for their mixtures. These broad peaks could be rationally assigned to the CT absorptions originating from the charge transfer between **PBDV** and DAN. Their absorption intensity increased as the number of DAN unit in the oligomers increased, indicating that the donor-acceptor interaction between them was enhanced by multiple donor-acceptor interaction sites as well as synergistic effect. Such trend could also be deduced by the observation of the color change upon mixing **PBDV** and donor oligomers, which varied from light yellow (with $\mathbf{D_1}$) to deep purple (with $\mathbf{D_4}$) with the increase of the number of DAN unit in the oligomers (Figure S6, ESI).

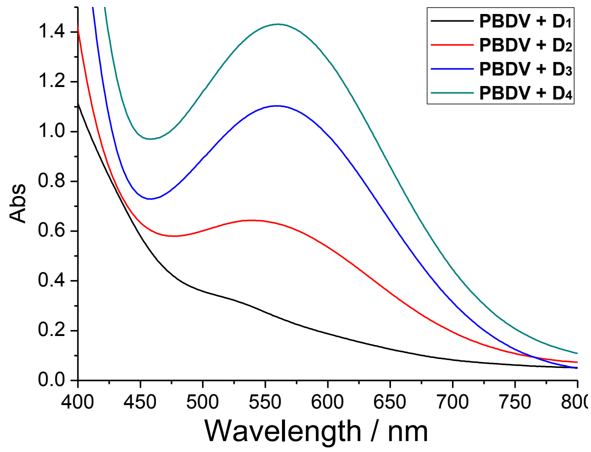


Fig. 2 UV-vis spectra of solutions of **PBDV** with $\mathbf{D_1}$-$\mathbf{D_4}$ in $CH_3CN/CHCl_3$ (4:1) at 20°C. The concentration of **PBDV** was 3.0 mM and the molar ratio for **PBDV** and the oligomers was 1:1.

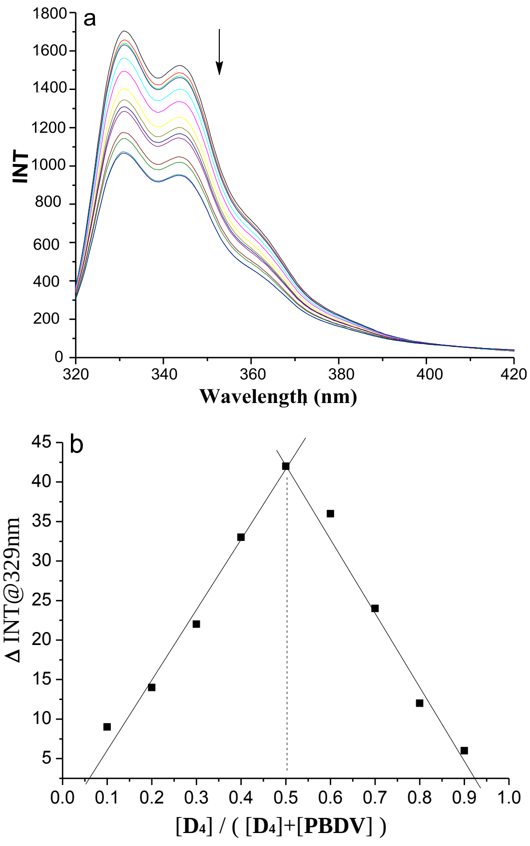


Fig. 3 (a) Fluorescence titration spectra of $\mathbf{D_4}$ (1.0×10^{-8} M) with **PBDV** (0 to 5.0×10^{-8} M) in CH_3CN at 25°C. Excited at 290 nm. (b) The Job's plot of **PBDV** with $\mathbf{D_4}$ generated by using fluorescence emission.

In order to get more insight into the supramolecular donor-acceptor complexes formed in solution, fluorescence experiments were further performed. First of all, the fluorescence emission intensities of oligomers $\mathbf{D_1}$-$\mathbf{D_4}$ were recorded at different concentrations, respectively (Figure S7, ESI). Their plots of intensity-concentration displayed a linear relationship, suggesting that the intermolecular interactions between the DAN units in the oligomers were negligible. In the next step fluorescence titration experiments of $\mathbf{D_1}$-$\mathbf{D_4}$ with

Table 1. Binding constants between **PBDV** and the DAN oligomers.[16]

	PBDV + D_1	**PBDV + D_2**	**PBDV + D_3**	**PBDV + D_4**
K_a / M^{-1}	$(7.13 \pm 0.06)\times10^2$	$(5.16 \pm 0.07)\times10^3$	$(1.55 \pm 0.03)\times10^4$	$(3.84 \pm 0.08)\times10^4$

Calculated from B-H plots by fitting the UV-*vis* titration data of DAN oligomers with **PBDV** in $CH_3CN/CHCl_3$ (4:1) at 25°C.

PBDV were carried out. Upon incremental introduction of **PBDV** into the solutions of the oligomers, the fluorescence emission of DAN was gradually quenched (Figure 3a and S8 in SI). Job's plots were generated by using fluorescence spectroscopy, which indicated a stoichiometry of 1:1 for **PBDV** and the oligomers (Figure 3b and S9). The binding constants (K_a) between **PBDV** and the DAN oligomers were estimated from Benesi-Hildebrand (B-H) plots[17] by fitting their UV-vis spectroscopic titration data (Figure S10). The results are provided in Table 1, which revealed that the K_a value of the complex formed between **PBDV** and **D_4** was about 54 times larger than that of the complex formed between **PBDV** and **D_1**, indicating again that the stability of complexes increased with the increasing number of DAN unit, as a result of the multivalent donor-acceptor interactions and the synergistic effect.

On the basis of the above results, the formation of stable complexes from **PBDV** and DAN oligomers **D_1-D_4** in 1:1 stoichiometry driven by donor-acceptor interactions between **PBDV** and DAN, could be confirmed. We anticipated that the flexible DAN oligomers adopted folded or helical conformations by wrapping on the rigid rod-like **PBDV**. In order to get the exact structures of the supramolecular complexes, we tried to grow their single crystals suitable for X-ray crystallographic analysis. However, all the attempts to grow single crystals were unsuccessful. As an alternative, DFT calculations at the B3LYP/6-31G level for optimized structures were conducted to gain insight into their structural features. To obtain the energy minimum folded/helical conformations, Monte Carlo conformational searches were firstly carried out to explore possible folded/helical structures which could be generated by **PBDV** and each DAN oligomers. For each case, a total of 20,000 structures were accumulated and the ten lowest-energy conformers were further optimized by DFT calculations with Gaussian 09 package at the B3LYP/6-31G level without consideration of solvation. In this way, several energetically minimized representative structures were obtained for each complex (Figure S10-13, ESI). Among these structures, the energetically lowest ones are illustrated in Figure 4 from different views. For the complex formed from **PBDV** and **D_1**, the energetically lowest optimized structure was the one in which two DAN units acted as a molecular tweezer to clip the pyridazine ring of **PDBV** (Figure 4a). In the case of **PBDV** and **D_2**, the whole donor oligomer twined round the backbone of **PBDV** to adopt a helical conformation, in which all the four DAN units stacked on the aromatic ring of **PBDV** in a face-to-face manner to form a helical structure.

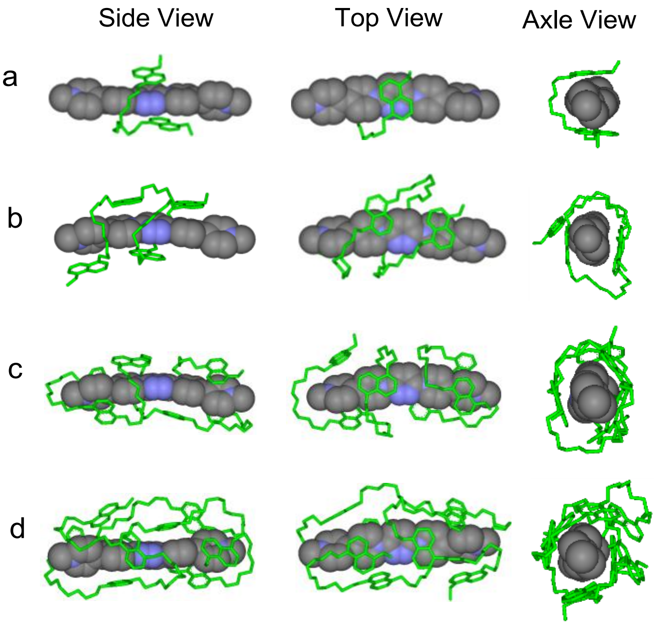


Fig. 4 The optimized energetically lowest structures of the complexes formed between **PBDV** and (a) **D_1**, (b) **D_2**, (c) **D_3**, and (d) **D_4** which were generated by DFT calculations at B3LYP/6-31G level.

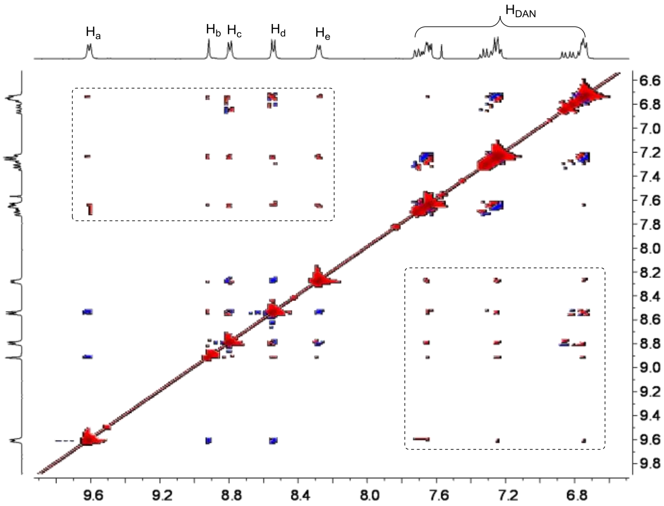


Fig.5 Partial 2D NOESY spectrum of **PBDV** + **D_4** in $CD_3CN/CDCl_3$ (4:1, 3.0mM).

In the case of **PBDV** and **D_3**, as the donor oligomer extended to include six DAN units, its flexible chain was induced by the rigid linear backbone of **PBDV** to wrap round **PBDV**, driven by the strong stacking between all the six DAN units and the aromatic ring of **PBDV** (Figure 4c). However, complex formed from **PBDV** and **D_4** displayed some difference from the above ones. As revealed by the simulations (Figure 4d), although a helical structure of the donor oligomer still generated under the induction of **PBDV**, the arrangement between **PBDV** and DAN units is different from the above complexes because the space on the both sides of the aromatic ring of **PBDV** was too congested to accommodate the eight DAN units of **D_4** for the stacking between them. Alternatively, some of the DAN units were sticking to the side of **PBDV** to form C-H···π interactions. In all the cases, it should be noted that the C-H···O hydrogen bonding between the hydrogen atoms of the pyridinium moieties of **PBDV** and the oxygen atoms of oligo-oxyethylene linkers in **D$_1$-D$_4$** may act as a second force to stabilize the helical folding supramolecular structures.[18]

The formation of folded and helical structures of **D$_1$-D$_4$** induced by **PBDV** was further supported by 2D ^{1}H NMR NOESY experiments. The NOESY spectrum of the 1:1 mixture of **PBDV** and **D$_4$** is provided as a representative (Figure 5). As revealed in Figure 5, significant intermolecular NOE connections (in the dashed box region) were observed between all the aromatic protons of **PBDV** and protons of DAN units of **D$_4$**, clearly indicating that they approached each other in a very close distance, which is consistent with the helical structure as illustrated in Figure 4d. The NOESY spectra of the other complexes (Figures S15-S17, ESI) displayed similar through-space correlations, also suggesting the formation of the wrapped structures between **PBDV** and **D$_1$-D$_3$**.

Conclusions

In summary, a rigid rod-like electron-deficient acceptor molecule and a series of electro-rich flexible linear donor oligomers have been designed and synthesized. Upon mixing the acceptor and each of the donors, the flexible linear oligomers could be induced by the acceptor to adopt folded or helical conformations through twining round the skeleton of rod-like acceptor in 1:1 stoichiometry, driven by donor-acceptor interaction. While currently most foldamers are constructed by internal induction of the folded structure through intramolecular interactions, this work demonstrates that the construction of folded/helical architectures by means of the induction of external templates is also an efficient approach. Although in the present work the folded/helical structures of the donor oligomers will collapse once the template is removed, this issue could be addressed by designing linear oligomers that can be post-cross-linked the as-formed secondary structures. In such way, the hierarchy of the structures can be retained even the template is removed. In this context, the externally inducing approach should also be a very promising approach to fabricate complicated artificial secondary structures.

Acknowledgements

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